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Upgrading of waste biomass by hydrothermal carbonization (HTC) and low temperature pyrolysis (LTP): A comparative evaluation

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HIGHLIGHTS

- The performance of HTC and LTP was compared to produce solid fuel from waste biomass.
- Fuel qualities of the biochars produced from HTC and LTP were investigated.
- Ash problem related metal contents in two biochars were analyzed.
- Combustion characteristics of two biochars were determined.
- Hydrothermally prepared biochar is suitable for use as a solid fuel.

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ABSTRACT

Hydrothermal carbonization (HTC) and low temperature pyrolysis (LTP) were compared on the basis of fuel qualities of biochars obtained from the upgrading of raw biomass in the present study. The results showed that the hydrothermally prepared biochar had higher energy density while the pyrolytic biochar had higher energy yield due to higher biochar yield. Nearly 100% major ash-forming metals were retained in the pyrolytic biochars while the contents of these metals in hydrothermally prepared biochars were less than 40% relative to those of raw biomass, especially for Na and K (less than 11% retention rate). The reactivities of pyrolytic biochars were higher than their respective raw biomass and the main mass loss occurred at low temperatures. The higher combustion temperature ranges and sharply decreased residue suggested that higher thermal efficiency and lower pollutant emissions could be achieved with the hydrothermally prepared biochars than with pyrolytic biochars. As for the process kinetics, HTC showed lower activation energy in the temperature range of 150–300 °C in spite of deeper decomposition and carbonization of biomass as compared to LTP.

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1. Introduction

Biomass resource used as a solid fuel for power and heat generation is viewed as an efficient option for energy recovery from renewable biomass. However, raw biomass is not suitable for direct combustion as it has several technical constraints which are associated with inherent properties of biomass materials, for example, low energy density and high moisture content [1]. Therefore, it is imperative to pre-treat the biomass to improve its fuel quality prior to combustion. Low temperature pyrolysis (LTP) and hydrothermal carbonization (HTC) are two principal thermal approaches to upgrade biomass feedstocks to accommodate the existing coal-fired boiler or furnace [2–4]. For LTP, biomass feedstock is heated under inert atmosphere with low heating rate and the target fuel in the form of pyrolytic biochar with improved fuel quality is generated. HTC simulates natural coalification in coal petrology, involving the decomposition and carbonization of biomass material in water medium at desired temperature and autogenous pressure [5]. No drying process is needed for HTC, which represents a practical advantage for biomass feedstocks as they are characterized by high moisture content. Both LTP and HTC of biomass feedstocks produce the biochars with improved fuel quality relative to raw biomass such as increased grindability and elevated energy density [3,4]. The increased grindability means the low energy consumption for biomass grinding and the elevated energy density reduces the operating cost for the handing logistics.

Extensive research has been conducted on biomass upgrading by these two approaches, with an aim to investigate the reactions mechanisms involved and optimize operation conditions [4,6–8]. Most of these research has focused on woody biomass, instead of

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abundant agricultural residues [4,9,10]. For example, loblolly pine was treated by HTC and LTP and the resultant biochars showed increased fixed carbon content and elevated energy density [4]. As a solid fuel, one of the key concerns in utilizing biomass feedstocks for energy generation is the occurrence of ash-related problems in boilers [11,12]. Biomass materials, especially agricultural residues, are known to be rich in alkali metals such as Na and K and these alkali metals can cause undesirable slagging and fouling in the high temperature furnaces and boilers due to the formation of low melting- or softening-point alkali silicates [1,13]. Moreover, the ash content and its chemical composition of solid fuel also have an influence on the application of combustion technology and the later ash disposal. Therefore, during pre-treatment the fate of the metals contained in raw biomass, especially those closely related to ash problems, is a key concern as it controls the performance of the subsequent combustion performance of resultant biochars. It has recently been reported that some inorganic components contained in raw biomass can be leached into the water medium during HTC process, leading to decreased ash contents in hydrothermally produced biochar relative to its parent biomass [3]. However, no detailed information is available in the literature on the distribution of metal species, especially those mainly related to ash problems, after HTC and LTP of biomass feedstocks up to date.

In addition, the knowledge of reaction kinetics is vital to design and operate the waste biomass-to-energy conversion reactors efficiently. Different decomposition reactions occur for biomass feedstocks during the course of HTC and LTP. Therefore, kinetic analysis should be performed to gain a better understanding of the relative performance of both HTC and LTP. Although the kinetics of biomass pyrolysis has been widely studied, that of HTC is scarcely reported in the literature [14–18].

The objective of this preliminary study is to make a comparative evaluation of the performance of HTC and LTP for conversion of biomass feedstocks to biochars by (1) investigating the contents of metals prior to and after HTC and LTP of biomass feedstocks and energy analysis of resultant biochars; (2) evaluating fuel qualities of the two biochars based on combustion analysis and (3) determining the kinetic parameters to better understand the upgrading of biomass by HTC and LTP processes. The ultimate goal of this work is to develop a viable pre-treatment process to produce solid fuels with improved fuel quality from biomass feedstocks while maintaining relatively high energy recovery rate and less energy consumption.

2. Experimental

2.1. Biochars preparation

Coconut fibers (CF) and eucalyptus leaves (EL) were selected as model raw biomass feedstocks for biochar production and their ultimate analysis is shown in Table 1. Based on the earlier findings reported in the literature [3,8,16], the biochars produced at 250 °C were used for various investigations in the present study. Fig. 1 shows the schematic diagrams of HTC and LTP reactors for biomass upgrading. A laboratory scale semi-batch 500-ml Parr autoclave reactor (USA) was used for the production of hydrothermal biochar and the detailed description of HTC can be found elsewhere [3]. The LTP of the biomass was conducted in a horizontal fixed-bed quartz reactor (60 mm i.d., 800 mm length). The biomass sample was loaded into an alumina boat which was then placed in a quartz tube and argon gas was introduced to maintain an inert atmosphere in the experimental system. The furnace was heated to the 250 °C at a heating rate of 20 °C/min and kept at this final temperature for 20 min, before cooling it down to room temperature. The biochars produced from HTC and LTP were designated as HC and PY, respectively. For example, CF-HC and CF-PY refer to the biochar produced from HTC and LTP of CF, respectively. All the raw biomass and biochars were dried at 105 °C for 24 h for subsequent analysis. The biochar yield and energy yield are defined as follows:

$$\text{Biochar yield} = \frac{\text{Mass of the biochar}}{\text{Mass of the raw biomass}} \times 100\% \quad (1)$$

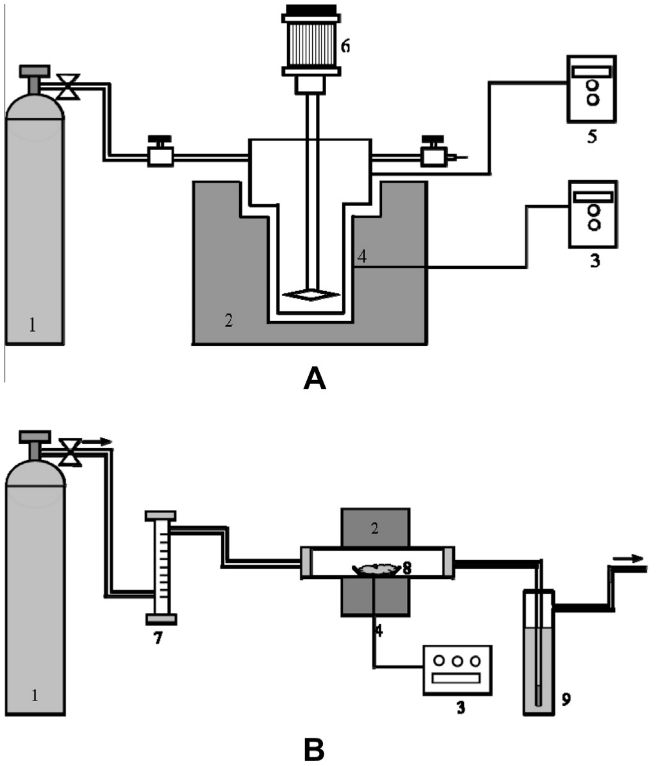

Fig. 1. Schematic diagrams of (a) HTC reactor and (b) LTP reactor for biomass upgrading (1: N_2 cylinder, 2: Heater, 3: Temperature controller, 4: Thermocouple, 5: Pressure meter, 6: Stirrer, 7: Gas meter, 8: Alumina boat, and 9: Gas trap).

Table 1
Ultimate analysis and energy analysis of hydrothermal and pyrolytic biochars produced from CF and EL.

	Ultimate analysis (%)					Energy analysis		
	C	H	S	N	O[a]	Biochar yield (%)	HHV (MJ/kg)	Energy yield (%)
CF	47.75	5.61	0.23	0.90	45.51	–	19.2	–
CF-HC	67.10	5.20	0.29	0.98	26.43	45.3	28.4	67.0
CF-PY	53.77	4.76	0.28	1.13	40.06	69.2	21.5	77.5
EL	46.96	6.22	0.77	1.23	44.82	–	18.9	–
EL-HC	62.30	5.47	0.44	1.44	30.35	46.4	25.8	63.3
EL-PY	49.83	5.77	0.90	1.28	42.22	72.2	20.3	77.6

[a] By difference.

$$\text{Energy yield} = \text{Biochar yield} \times \frac{\text{Energy content of the biochar}}{\text{Energy content of the raw biomass}} \qquad (2)$$

2.2. Biochars characterization and kinetic study

Elemental analysis (C, H, N and S) of the fuel was determined using Vario Macro Cube Elementar (Germany) and oxygen was calculated by difference. The higher heating value (HHV) of the fuel was measured with a Kaiyuan 5E-KC5410 Express Calorimeter (China). The fuel sample was combusted in an oxygen-rich environment inside a bomb that was contained within a water bath. The increase in temperature of the water bath was used to calculate the HHV of the fuel sample. The infrared spectrum (as KBr disk) was recorded in the wavenumber range of 4000–600 cm^{-1} with a Nicolet Nexus 670 Spectrophotometer (USA) at room temperature. As for the contents of metals in biomass/biochars, the fuel was digested using a mix of acids with hydrogen peroxide (2 ml 65% HNO_3, 2 ml 30% H_2O_2 and 0.5 ml 48% HF) at 180 °C for 30 min using a microwave digester (Milestone, USA). The digestion solution was then evaporated to dryness to remove the fluorides and the resultant residues were dissolved in HNO_3 solution, followed by dilution by de-ionized water to desired volume. Subsequently the metal concentrations (K, Na, Ca, Fe, Si, Al, Ti and Mg) in the solution were quantified by inductively-coupled plasma optical emission spectrometer (ICP–OES Perkin Elmer 3000DV (USA)).

A thermobalance TGA-Q500 (USA) was used for kinetic study of LTP of biomass and evaluation of combustion properties of the biochars. The kinetic study of LTP was carried out under nitrogen atmosphere at a linear heating rate of 15 °C/min. All combustion experiments were conducted at atmospheric pressure, using temperatures ranging from room temperature to 800 °C with a heating rate of 20 °C/min and an air flux of 30 ml/min. To minimize the effects of mass and heat transfer limitations, very small sample sizes (around 8 mg) were loaded into an alumina crucible.

The first-order kinetics is most frequently assumed for solid fuel decomposition, and hence was used in this study to evaluate the HTC and LTP of biomass [15,19,20]. The kinetic equation can be described by the following formula:

$$\ln\left[-\frac{\ln(1-a)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \qquad (3)$$

where E is apparent activation energy; A is pre-exponential factor; T is absolute temperature; R is the gas constant; and a and β are mass loss and the heating rate, respectively.

If HTC and LTP of biomass follow the first-order reaction mechanism, then the plot of $\ln[-\ln(1-a)/T^2]$ versus $1/T$ is expected to give a straight line. From the slope, E/R, the apparent activation energy can be obtained and by taking the absolute temperature at which half conversion rate is achieved, the pre-exponential factor A can be calculated.

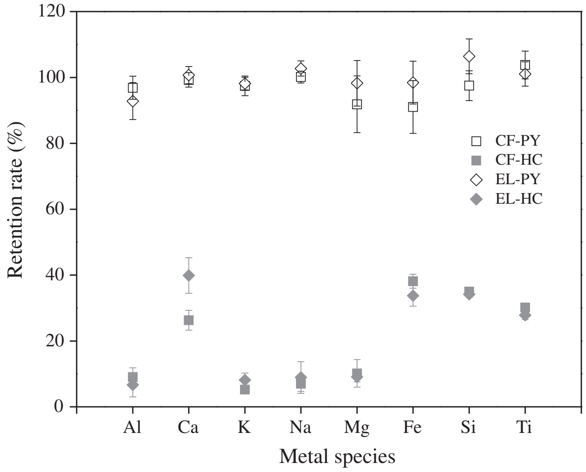

Fig. 2. Metal retention rates in hydrothermal and pyrolytic biochars produced from CF and EL.

3. Results and discussion

3.1. Energy analysis and major ash problems related metals analysis

As shown in Table 1, compared to hydrothermally prepared biochars, pyrolytic biochars have higher yield, 69.2% and 72.2% for CF-PY and EL-PY. The lower yields of hydrothermally prepared biochars together with the higher HHVs imply that the biomass underwent a deeper decomposition and carbonization under HTC in comparison with LTP. This also was confirmed by the ultimate analysis: higher carbon contents and lower oxygen contents of hydrothermally prepared biochars relative to pyrolytic biochars. Due to the higher biochar yields, the pyrolytic biochars exhibited higher energy yields in spite of lower HHVs in comparison with those of hydrothermally prepared biochars.

Table 2 shows various metals contents of raw biomass and the corresponding biochars. These metals are mainly associated with ash-related problems including the slagging and fouling during the combustion of a solid fuel. In both CF and EL, Ca and K are the dominant metals (Ca and K are 0.33% and 1.60%, and 2.28% and 0.66% for CF and EL, respectively) and the contents of some metals such as Al and Ti are very low. The HTC of biomass resulted in significantly decreased metal contents in hydrothermal biochars, while the metal contents dramatically increased in the corresponding pyrolytic biochars. For example, K and Na, which are most concentrated in biomass fuels, were decreased by higher than 80% in hydrothermally prepared biochars in comparison to the raw biomass (CF-HC/CF: K 11.50%, Na 15.45%; EL-HC/EL: K 17.52%, Na 19.23%). In contrast, these two metal contents were drastically increased in pyrolytic biochars (CF/CF-PY: K 71.02%, Na 69.10%; EL/EL-PY: K 73.56%, Na 70.27%).

The retention rate of the metal was defined as the percentage of the metal content in biochar accounting for the metal content in raw biomass. Fig. 2 shows the retention rates of the tested metals

Table 2
Ash problems related metals contents for CF and EL, and their corresponding hydrothermal and pyrolytic biochars.

	Ca (%)	K (%)	Al (%, ×10)	Na (%, ×10)	Mg (%, ×10)	Fe (%, ×10)	Si (%, ×10)	Ti (%, ×10)
CF	0.33	1.60	0.05	1.23	0.58	0.19	0.22	0.07
CF-HC	0.19	0.18	0.01	0.19	0.13	0.16	0.17	0.04
CF-PY	0.47	2.25	0.07	1.78	0.77	0.25	0.31	0.09
EL	2.28	0.66	0.07	0.26	0.97	0.11	0.19	0.05
EL-HC	1.96	0.12	0.01	0.05	0.19	0.08	0.14	0.03
EL-PY	3.18	0.90	0.09	0.37	1.32	0.15	0.28	0.07

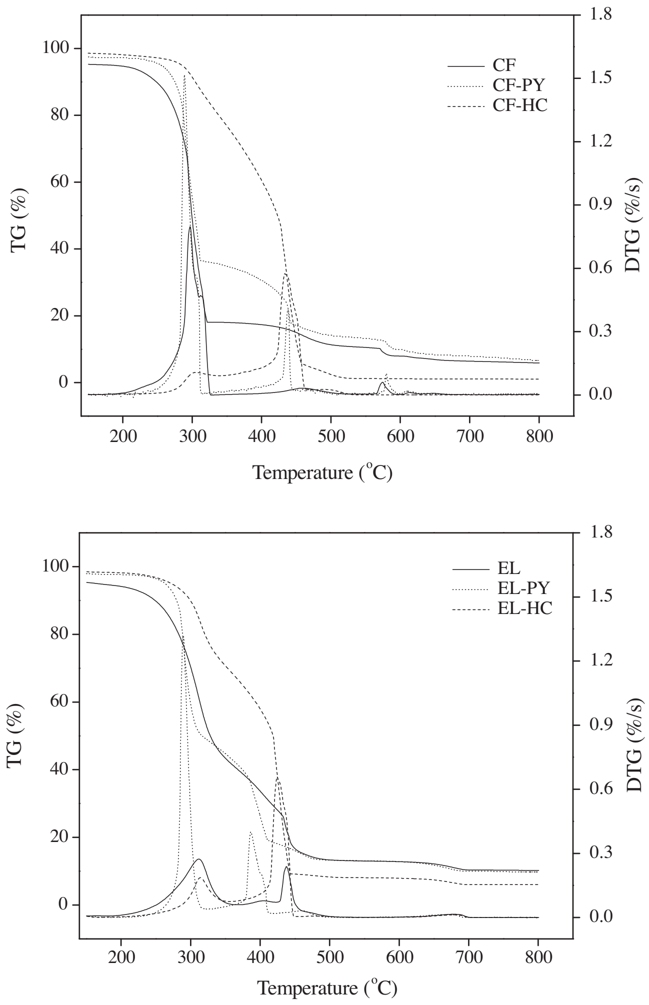

Fig. 3. TG and DTG curves for the combustion of CF, EL and their derived hydrothermal and pyrolytic biochars.

after HTC and LTP. It was obvious that all the metals in raw biomass were around 100% retained in the pyrolytic biochars during LTP while for HTC, the retention rates in hydrothermally prepared biochars were less than 40% for all the metals. The lowest retention rates were Na (6.99%) and Al (6.63%) for CF and EL after HTC, respectively. In addition, it was worth noting that light and heavy metals exhibited noticeably different retention rates during HTC. For the light metals, Al, K, Na and Mg, the retention rates were as low as less than 11.0% while for the heavy metals including Fe, Si and Ti, relatively higher retention rates were observed (higher than 27.8%). During HTC, the highest retention rates were observed for Fe (38.1%) and Ca (39.9%) for CF and EL, respectively.

This observation can be ascribed to the difference in the inherent properties between light and heavy metals, and the existence of their different chemical forms in the raw biomass.

In contrast to light metals, heavy metals have strong hydrolysis tendency and the hydrolysis reaction can probably occur under HTC conditions. The hydrolysis products precipitate from the water medium and then mix with the hydrothermal biochar. Even the heavy metals cannot hydrolyze thoroughly, the heavy metal also has strong co-ordination ability and they can coordinate with the increased functional groups on the surface of the hydrothermally prepared biochars, resulting in high retention rates [21]. In addition, different chemical forms of light and heavy metals in raw biomass could have also contributed to the different retention rates during HTC. For example, substantial amount of heavy metals such as Fe and Ti are known to exist as oxyhydroxides and silicates, and some heavy metals are present even in the form of crystal inorganics those generally have low solubility [22]. In contrast, for the light metals such as K and Na, they are in the form of water solubility in raw biomass resource and even washing can efficiently remove them from raw biomass. For example, up to 92% of Na and 62% of K were removed from herbaceous biomass by water washing [23].

Currently, the indices used for evaluating ash-related problems of a solid fuel including the fouling and slagging tendency are from the fuel ash analysis, instead of direct fuel sample [24,25]. Therefore, to determine the fouling and slagging tendency of two biochars, it is necessary to further carry out the ash analysis. However, from the significantly decreased alkali metals contents and less significantly decreased Si and Ti contents (decreased base-to-acid ratio), the mitigated fouling and slagging tendency were expected for the combustion of hydrothermally prepared biochars. In contrast, nearly 100% metal retention rates and increased sulfur content of pyrolytic biochars, the ash related problems were even more serious for pyrolytic biochars than that of raw biomass.

It has been reported that LTP combined with washing pretreatment produced the biochars with low ash content and improved fuel quality [23]. Except the use of chemicals, extensive energy was also consumed for the drying process during subsequent combustion. Therefore, HTC was able to potentially mitigate the ash-related problems and significantly upgrade biomass feedstocks while maintaining relatively low energy consumption in comparison with LTP.

3.2. Combustion characteristics

The TG and DTG profiles of raw biomass, pyrolytic biochars and hydrothermally prepared biochars are shown in Fig. 3. For clarity, the mass loss of biomass at temperatures lower than 150 °C caused by the evaporation of the moisture for both CF and EL is not shown. Table 3 presents the corresponding combustion parameters for each fuel obtained from TG and DTG analysis.

As can be seen in Fig. 3, the combustion characteristics of EL were quite different from those of CF. There were two stages for the mass loss during EL combustion, corresponding to the peak temperature at 312 and 438 °C, respectively. For CF, only one main stage was observed centered at 297 °C with around 77% mass loss occurring in the temperature range of 176–327 °C. For DTG curves,

Table 3
Combustion parameters of CF, EL and their corresponding hydrothermal and pyrolytic biochars.

	Temperature interval (°C)		Mass loss (%)		Peak temperature (°C)		DTG_{max} (%/s)		Residue (%)
	Stage I	Stage II	Stage I	Stage II	Stage I	Stage II	Stage I	Stage II	
CF	176–327		77		297		0.79		5.92
CF-HC	151–342	342–532	19	78	304	436	0.11	0.58	1.02
CF-PY	175–424	421–562	47	35	289	437	1.51	0.40	6.19
EL	183–374	374–555	56	25	312	438	0.27	0.24	10.23
EL-HC	180–360	360–452	30	59	315	425	0.18	0.66	5.78
EL-PY	200–320	320–415	46	29	290	386	1.32	0.40	9.77

the combustion of EL took place in two separated temperature ranges: 183–374 °C and 374–555 °C. The first temperature range with the maximum mass loss rate (DTG_{max}) 0.27%/s was due to the decomposition and devolatilization of less complex constituents and the second temperature range with DTG_{max} 0.24%/s corresponded to thermal decomposition/oxidation of more complex constituents including char gasification and combustion of fixed carbon. For CF, the combustion occurred only within one temperature range from 176 to 327 °C with higher DTG_{max} 0.79%/s. The minor peak appearing at 565–595 °C was ascribed to the decomposition of inorganic matters contained in CF.

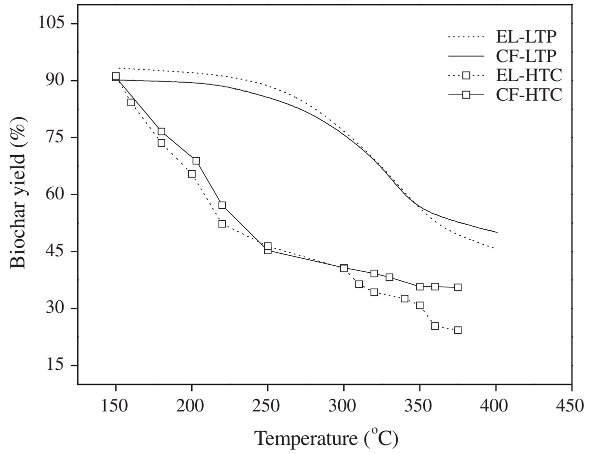

Fig. 4. Biochar yields as a function of temperature for CF and EL under HTC and LTP.

As in EL, the combustion of EL-PY still took place in two separated temperature ranges: 200–320 °C and 320–415 °C. Compared to EL, however, the peak temperatures decreased to 290 and 386 °C and the corresponding DTG_{max} increased to 1.32 and 0.40%/s at two respective temperature ranges. Furthermore, the mass loss in the first temperature range decreased to 46% in EL-PY as compared to 56% in EL combustion. For CF-PY, the low combustion temperature range was similar to that of CF, while a higher combustion temperature range appeared within the range of 421–562 °C. Similar to EL-PY, the DTG_{max} of CF-PY was remarkably increased by 91% to 1.51%/s from 0.79%/s in CF combustion at the low temperature range. A significant decrease was also observed for the mass loss from 77% for CF to 47% for CF-PY.

For CF-HC and EL-HC, the combustion took place in two temperature ranges while main mass loss shifted to higher temperature range: 78% for CF-HC at temperature range of 342–532 °C and 59% for EL-HC at temperature range of 360–452 °C. There was significant decrease for the DTG_{max} of hydrothermally prepared biochars at low temperature range compared to those of pyrolytic biochars and raw biomass. Furthermore, HTC narrowed the two combustion ranges, i.e., CF-HC and EL-HC combusted in a relatively continuous temperature range.

In addition, from TG curves, the pyrolytic biochars had comparable residue to those of raw biomass while there was a significant decrease of the residue for hydrothermally prepared biochars (decreased by 82.77% and 43.50% for CF-HC and EL-HC, respectively). The decreased residues of hydrothermally prepared biochars confirmed that the part of inorganic composition of raw biomass entered water medium under HTC conditions and were well consistent with metals content analysis. Also, the DTG peak cen-

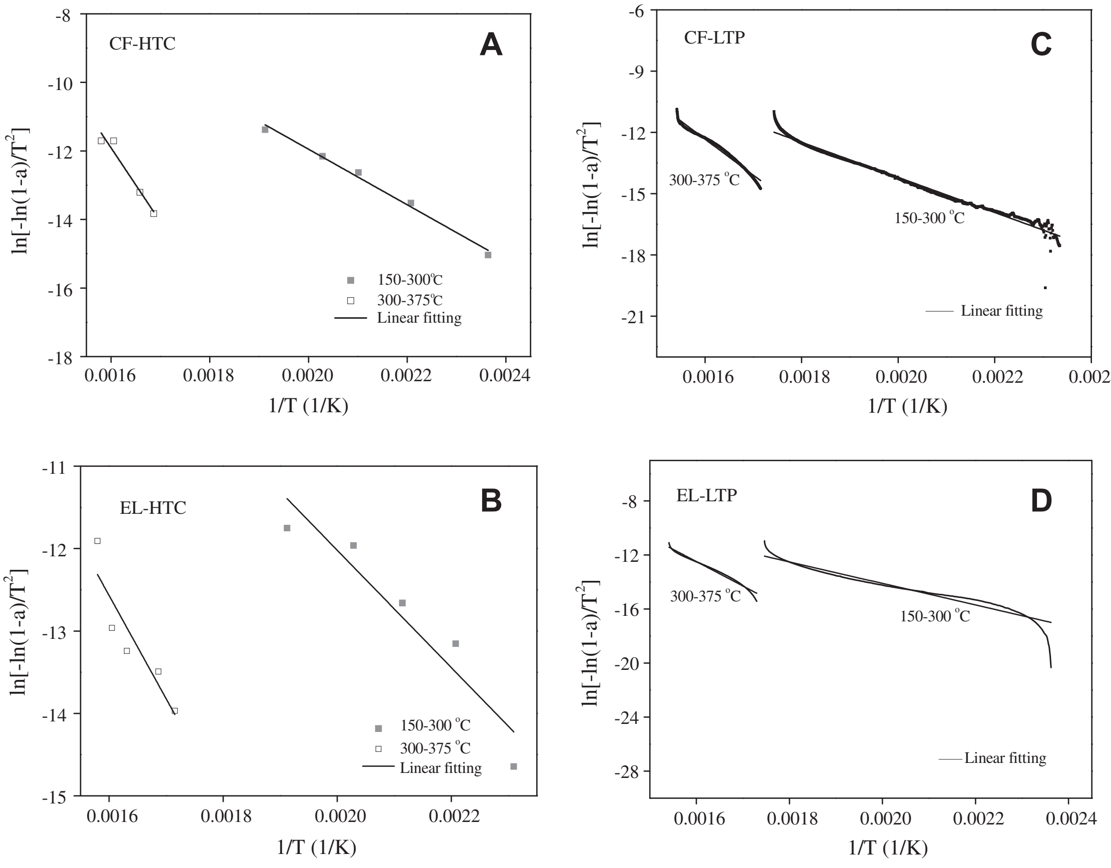

Fig. 5. Linear fitted plots for HTC and LTP of CF and EL using Coats–Redfern method within two separated temperature ranges (range 1: 150–300 °C and range 2: 300–375 °C).

tered at around 580 °C in CF and CF-PY disappeared in that of CF-HC and this observation was agreed with above analysis.

Taking into account that the temperature value at the $\mathrm{DTG}_{\max}$ is considered inversely proportional to the reactivity of fuel [26], the biochars produced from HTC and LTP had totally different reactivities: increased reactivities for pyrolytic biochars and decreased reactivities for hydrothermally prepared biochars. The decreased reactivity of hydrothermally prepared biochar was mainly ascribed to low contents of light metals (especially K), which were reported to catalyze the pyrolysis of biomass [23,27]. According to above mental content analysis, all the metal species in the hydrothermally prepared biochars were significantly lower than those in raw biomass; for example, the K content of CF-HC was around 11.25% relative to that of CF. In contrast, all the metals were enriched in pyrolytic biochars; for example, the content of K was increased by 40.81% and 35.95% in CF-PY and EL-PY relative to that in CF and EL, respectively.

The lower combustion temperature and the non-continuous combustion temperature ranges of raw biomass are associated with higher pollutant emissions and lower thermal efficiency. The elevated combustion temperature and continuous combustion temperature ranges indicated that the fuel quality of raw biomass was significantly improved by HTC at 250 °C. However, from the combustion analysis of pyrolytic biochars, it was observed that the fuel quality was not enhanced substantially by LTP, especially for EL, in the present study.

3.3. Kinetic analysis of HTC and LTP

As shown in Fig. 4, the biochar yield decreased significantly with elevated temperature in the range of 150–300 °C, and further decreased up to 375 °C under HTC in the present study. The reaction rates were different above or below 300 °C, therefore, the temperature range was divided into range 1 (150–300 °C) and range 2 (300–375 °C), and the kinetic parameters were calculated separately within these two distinct temperature ranges.

Plots of $\ln[(-\ln(1-a)/T^2)]$ against $1/T$ are shown in Fig. 5A and B and the regression functions were obtained by a linear fitting method. The high correlation coefficients (R^2, presented in Table 4) indicated that the first-order reaction mechanism well described HTC of CF and EL within both temperature ranges. There were significant differences for the apparent activation energies of HTC in the different temperature ranges for both CF and EL. The CF had activation energies of 67.5 and 179.5 kJ/mol while the EL had 59.2 and 173.7 kJ/mol for temperature ranges 1 and 2, respectively. From our previous structural analyses, hemicellulose decomposed first at lower temperatures (lower than 250 °C) followed by cellulose which decomposed completely at 300 °C under HTC [3]. For the lignin, at temperatures lower than 300 °C, only melting would occur instead of degradation. In the present study, the decomposition of hemicellulose and cellulose, and the decomposition/carbonization of lignin occurred primarily at lower temperatures (temperature range 1) and higher temperatures (temperature range 2), respectively. Therefore, the apparent activation energy of temperature range 1 was the combined activation energies of decomposition of hemicellulose and cellulose, while the activation energy of temperature range 2 was mainly applicable to lignin. As a result of the large difference between carbohydrates (hemicellulose and cellulose) and lignin, the reactions that occurred were

Table 4
The kinetic parameters for HTC and LTP of CF and EL.

Sample		Temperature (°C)	Equation	R^2	E (kJ/mol)	A
CF	HTC	150–300	$Y = -8107.5x + 4.27$	0.991	67.5	4.08E+12
		300–375	$Y = -21595x + 22.64$	0.955	179.5	1.23E+21
	LTP	150–300	$Y = -8598.5x + 2.99$	0.985	71.5	1.15E+12
		300–375	$Y = -17662x + 15.93$	0.978	146.8	1.44E+18
EL	HTC	150–300	$Y = -7118.1x + 2.22$	0.903	59.2	4.38E+11
		300–375	$Y = -20893x + 21.37$	0.992	173.7	2.05E+20
	LTP	150–300	$Y = -7982.6x + 1.86$	0.945	66.4	1.01E+12
		300–375	$Y = -18090x + 16.46$	0.982	150.4	2.53E+18

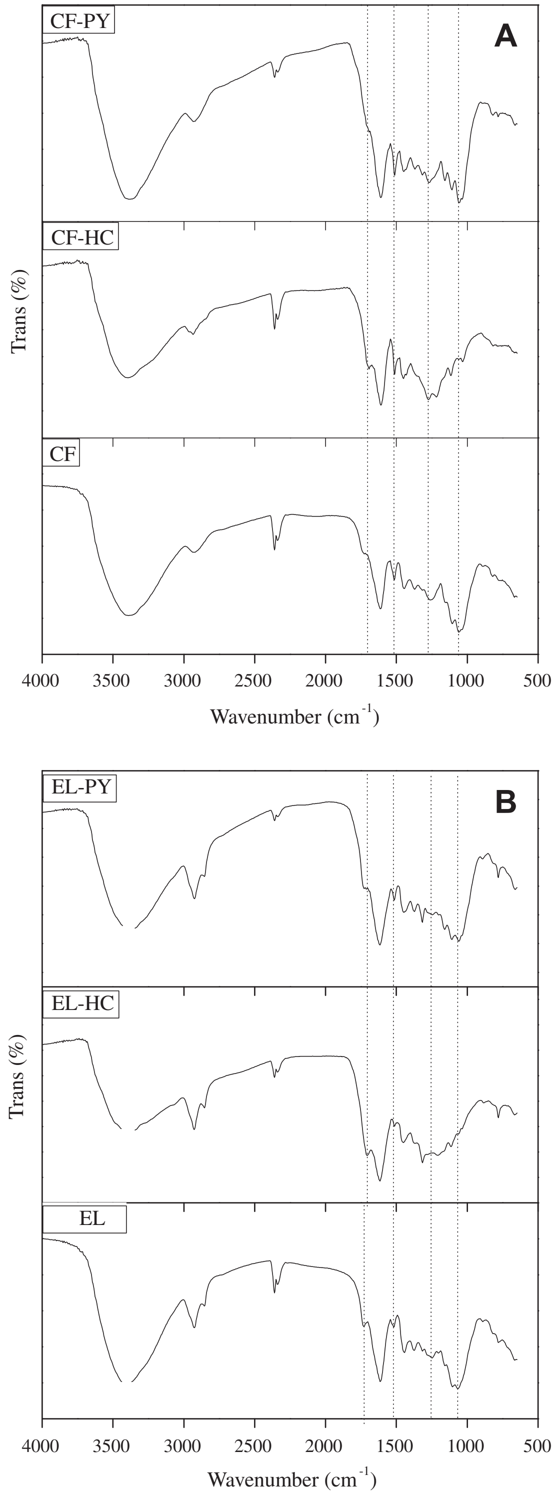

Fig. 6. FT-IR spectra of CF, EL and their derived hydrothermal and pyrolytic biochars.

quite different between temperature ranges 1 and 2, leading to different apparent activation energies. In addition, from the viewpoint of chemical reactions, competing reactions such as condensation, depolymerization, and polymerization occurred during the HTC of biomass. Depolymerization reactions are thought to dominate at low temperatures, while polymerization and aromatization reactions dominated at high temperatures [6,7]. As a consequence, different apparent activation energies resulted from the different reactions in these two temperature ranges.

As for the pyrolysis (shown in Fig. 4), the thermal decomposition of both CF and EL started around 200 °C followed by a major weight loss in the temperature range of 200–450 °C, during which the volatiles was released and the char was formed [28]. Considering that the HTC was only carried out in the temperature range of 150–375 °C, the two separated temperature ranges, namely, 150–300 °C and 300–375 °C, were also used to evaluate the reaction kinetics to get a direct comparison between HTC and LTP. Plots of $\ln[(-\ln(1-a)/T^2)]$ against $1/T$ were demonstrated in Fig. 5C and D and the higher correlation coefficients (R^2, presented in Table 4) indicted that the first order reaction mechanism also fitted well the LTP of CF and EL in the present study.

To get a direct comparison for structural evolution of biomass under HTC and LTP, FT-IR spectra of two types of biochar were conducted. As shown in Fig. 6, the main difference among the spectra of raw biomass, hydrothermally prepared biochars and pyrolytic biochars was the peak at 1064 cm^{-1} which was ascribed to the β-glycosidic bond in cellulose and hemicellulose [3]. As can be seen from Fig. 6, the intensity of this peak decreased significantly in hydrothermally prepared biochars, indicating that nearly all hemicellulose and cellulose decomposed under HTC. In contrast, limited decrease for this peak was observed in pyrolytic biochars. Considering the relatively higher decomposition temperature of cellulose, this result implied that only part of cellulose decomposed under LTP at 250 °C in the present study [18]. The peaks around 1513 cm^{-1} (C=C aromatic ring vibration) and 1262 cm^{-1} (aromatic C–O stretching of methoxyl and phenyl propane structure) were present in hydrothermal and pyrolytic biochars, indicating lignin did not degrade under both HTC and LTP conditions. The peak at around 1735 cm^{-1}, attributed to C=O stretching vibration of carboxylic acid in hemicellulose, disappeared in both biochars and the peak around 1699 cm^{-1} was ascribed to the degradation product of hemicellulose. This observation concluded that hemicellulose degraded under both HTC and LTP conditions in the present study. Therefore, the first temperature range of 150–300 °C mainly corresponded to the decomposition of hemicellulose possibly including part of cellulose under LTP. This result also confirmed that a deeper decomposition of biomass took place under HTC than LTP when carried out at the same temperature. Both HTC and LTP of CF and EL well fitted first order kinetics model in the present study, which could probably be attributed to the small particle size of starting materials and low heating rate [18,29,30]. Although the biomass underwent a deeper decomposition under HTC than LTP, the apparent activation energy of HTC was lower than that of LTP in the first temperature range. The lower activation energy and improved fuel quality of hydrothermally prepared biochars indicated the promising potential of HTC for the biomass upgrading.

4. Conclusions

The hydrothermally prepared biochars had higher energy contents while the pyrolytic biochars had higher energy yields. The metal contents decreased significantly in hydrothermally prepared biochars compared to raw biomass while the retention rates for all metals were around 100% in pyrolytic biochars. The combustion of pyrolytic biochars mainly occurred at low temperatures while that of the hydrothermally prepared biochars was shifted to a higher temperature range. In spite of a deeper decomposition of biomass under HTC than LTP at the low temperature range, the activation energy of HTC was lower than that of LTP. The low activation energy and significantly improved fuel qualities of hydrothermally prepared biochars indicated that the pre-treatment of biomass feedstocks by HTC was more favorable than by LTP for biomass upgrading.

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